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硕 士 学 位 论 文

高功率激光电离飞行时间质谱用于铁氧化物和钴氧化物的形态分析

High Irradiance Laser Ionization Time-of-Flight Mass
Spectrometry for Direct Speciation Analysis of Iron Oxides
and Cobalt Oxides

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摘 要

在人们的传统观念看来,对于待考察样品中元素的分析仅限于定性,半定量和定量。然而,随着科学技术日新月异的进步,人们的认识也在不断地提高,越来越多的科学工作者意识到对于许多元素而言,仅仅测定它们各自的总含量对于样品评估来说是远远不够的,甚至在某些情况下还会引起一些危害性的错误结论。关于元素砷的测定就是一个最好的例证:在很多海鲜中,元素砷主要是以无毒的有机砷化合物的形式存在;而无机砷相对则是带有剧毒性的,并且在某种程度上取决于砷的化合价。由此可见,元素的化学形态直接决定着它们的很多性质,例如毒性,生物、化学活性,环境效应,等等。因此,元素形态分析涉及的领域越来越广泛:无论是临床医学化学、环境科学,还是地质学、生物无机化学,乃至一些其他的学科,都将大量的科研精力投入到元素形态分析这一举足轻重并且具有重要意义的领域。

到目前为止,对大多数样品体系而言,元素形态分析的手段往往依赖于先分离后检测的溶液方法。通常,样品先被溶解,再根据其中组分的极性或带电性差异采用色谱或电泳技术分离,最后采用原子光谱方法(如原子吸收光谱 AAS、原子发射光谱 AES、原子荧光光谱 AFS)或者质谱(MS)方法对各个组分进行定性和定量。对于元素形态分析,这类联用方法虽然在检测限、选择性、稳定性方面有其独特的优势,然而溶液分析法因操作繁琐、耗时过长。容易引入外来污染,于是渐渐地淡出了人们的视野;此外由于这类方法往往需要加入外标,加之不能满足在线实时分析的需求,人们便将关注焦点更多地转向固体直接分析法。

在诸多的仪器分析法中,前人曾采用 X 射线荧光光谱(XRF)和质谱的方法进行过固体样品的直接形态分析。对于 X 射线荧光光谱法,通过研究元素荧光谱线的能量位移或者强度比值,可得到形态分析的结论。但是,由于荧光谱线能量、宽度和强度比值的相似性,该方法不能区别含有相同元素的氧化物和盐类。相反,若用质谱方法进行形态分析,便不会出现该问题,因为盐类、氧化物和含氧酸盐的质谱谱图很容易鉴别。可是,对于有些离子源的质谱方法,还是会存在一些明显的问题。例如在辉光放电质谱(GDMS)中,样品必须具有导电性,因此,对于不导电的样品往往需要加入分析纯的石墨或者金属粉末与其混合,这

样便增加了样品前处理的时间和成本；在二次离子质谱（SIMS）中，虽然对于样品的属性没有具体的要求，可是有限的离子产率、污染以及与整体样品化学计量比不一致的表面氧化层，都增加了形态分析的难度。因此，在二次离子质谱方法中，往往需要对样品表面进行预处理。

上述两种离子源质谱虽然可进行固体样品的直接形态分析，但因其各自存在的缺陷，在实际领域中的应用较为有限。因此，现今质谱用于固体分析更多的是与激光离子源联用。激光电离质谱作为一种强大的质谱分析手段，鉴于其功能多样化，应用范围和受欢迎程度明显优于辉光放电和二次离子质谱。截止到目前为止，质谱工作者们已经利用激光电离质谱做了一些氧化物中元素形态分析的杰出工作。但是，这些研究所采用的激光功率密度大多都低于 10^8 W/cm^2 ，这就意味着激光与样品之间的作用机理主要是先解吸再离子化的过程。在本论文中，我们采用自制改进的激光电离垂直引入式飞行时间质谱，在激光功率密度高于 10^{10} W/cm^2 的情况下，对铁氧化物和钴氧化物进行直接的金属元素形态分析，并且提出了可能与前人不是一样的离子化机理。

本论文主要包括以下几个方面的内容：

第一章介绍了元素形态分析的概念和意义，对目前存在的元素形态分析方法做了详细的概述，并提出了本课题的研究背景和深远意义。

第二章主要对实验室自制的激光电离垂直引入式飞行时间质谱的结构，原理，以及之后的改造过程作了详细的介绍。此外，激光与固体物质在不同能量下的作用机理亦是本章探讨的重点。

第三章介绍了高功率激光电离飞行时间质谱在铁氧化物形态分析中的应用，考察了激光波长，激光功率密度和离子源气压对实验结果的影响，提出了激光功率密度高于 10^{10} W/cm^2 时团簇离子的形成机理和使用团簇离子信号强度比值用于铁氧化物形态分析的方法，并结合激光解吸电离飞行时间质谱对铁氧化物进行形态分析的结果及前人的工作，展现出了本研究工作中高功率激光电离飞行时间质谱用于元素形态分析的优势。

第四章介绍了高功率激光电离飞行时间质谱对铁氧化物形态分析的仪器工作模式在研究钴氧化物时的可行性。并验证了团簇离子信号强度比值法在钴氧化物形态分析研究的通用性。

第五章总结了激光电离飞行时间质谱在金属氧化物形态分析领域的所做工作，分析了研究过程中存在的缺点和不足，并对未来需要展开的研究工作提出了展望。

关键词：元素形态分析；高功率激光电离；飞行时间质谱；铁氧化物；钴氧化物

Abstract

In people's traditional concept, elements detection only consists of qualitative, semi-quantitative and quantitative analysis. But with the rapid development of science and technology, people's awareness has been growing continuously. More and more scientific researchers begin to realize that for many elements, only determining total concentration is not enough, and sometimes leads to erroneous conclusions. The example of arsenic is just the case: in many types of seafood arsenic exists in the form of nontoxic organic arsenic while inorganic arsenic is highly toxic, and to a degree that depends on its oxidation state. Thus it can be seen that chemical speciation of elements directly influences their properties, such as toxicity, bioactivity, environmental impact, etc. As a result, elemental speciation analyses have been employed in a wide range of disciplines. No matter clinical and medicinal chemistry, environmental science, or geology, bioinorganic chemistry and others, has been devoting great effort in the very important area of elemental speciation analysis.

Up to now, for most sample system, speciation analysis of particular elements has been being conducted by solution-based analytical techniques. Normally, samples are firstly dissolved and separated by chromatography or electrophoresis depending on the differences in polarity or electrical property between various components. Later, qualitative or quantitative analysis of each component is conducted using atomic spectrometry such as atomic absorption, emission, fluorescence spectroscopy (AAS, AES, AFS), and mass spectrometry (MS). Although the hyphenated technique has unique advantage in the area of speciation analysis considering its detection limit, selectivity and stability, it has gradually fade out of people's field of vision because of trivial manipulation, long processing time, and the presence of foreign contaminants. Besides, as the hyphenated technique requires external standard and can not be used in real-time on-line analysis, methods involving direct analysis of solids attract the most attention.

Among various instrumental analysis methods, X-Ray fluorescence (XRF) and

MS were once used to conduct direct speciation analysis of solid samples. Using the XRF method, direct speciation could be carried out through investigation of energy shifts or intensity ratios of fluorescence lines. However, these methods are not able to distinguish oxides from salts because the detection of line energy, width, or intensity ratios lead to nearly identical results. In contrast, an MS method would not suffer from these problems, as the mass spectrum of binary salts, oxides, and oxysalts could easily be identified. Nevertheless, several obvious faults exist for some MS ionization methods. Conventional glow discharge mass spectrometry (GDMS) uses sample conductivity and requires analytical grade graphite or metal powder mixtures of insulative oxides, which increases the time and cost of sample preparation. Although there are no special requirements for sample properties in secondary ion mass spectrometry (SIMS) analysis, the limited sputtered ions, pollutants, or the superficial oxide layer, which is stoichiometrically different from the bulk, often make speciation analysis complicated. Thus, before the acquisition of SIMS data, a pre-sputtering step may be necessary.

Although MS with GD and SI ionization methods are able to conduct direct speciation analysis of solid samples, due to the each disadvantage, they were seldom used in practical area. Therefore, nowadays most MS is coupled with laser ionization method to analyze solid samples. As a powerful analytical technique and due to its versatility, laser ionization mass spectrometry (LIMS) has much wider range of application and is more welcome than GDMS and SIMS. Several excellent studies have been conducted on oxide differentiation by LIMS so far. However, the studies were conducted with laser irradiation less than 10^8 W/cm^2 , which indicates that the laser-target interaction mechanism probably involves a desorption-ionization process accompanied by the emission of isolated neutrals, ions, and electrons. In this thesis, with laser irradiation more than 10^{10} W/cm^2 , we conducted direct speciation analysis of metal elements in iron oxides and cobalt oxides using home-built laser ionization orthogonal time-of-flight mass spectrometer (LI-O-TOFMS). Also a potentially different ionization mechanism compared with the previous studies was shown.

The thesis mainly consists of the following contents:

Chapter 1 firstly introduces the concept and meaning of elemental speciation analysis, then detailedly summarizes the methods for speciation analysis at present, and presents the background and profound significance of this project.

Chapter 2 mainly conducts an introduction of the structure, principle and later modification, optimization process of the home-built LI-O-TOFMS. Besides, the interaction mechanism between laser and sample with different laser irradiation was discussed.

Chapter 3 shows the application of high irradiance LI-TOFMS in the speciation analysis of iron oxides. The influence of operating parameters such as laser wavelength, laser irradiance and pressure in ionization chamber on the distribution of cluster ions was investigated, and their mechanism of formation was discussed when laser irradiance is higher than $10^{10}\text{W}/\text{cm}^2$. The advantage of high irradiance LI-TOFMS for speciation analysis is obvious when compared with laser desorption TOFMS.

Chapter 4 shows the application of high irradiance LI-TOFMS in the speciation analysis of cobalt oxides. The method of ions ratio calculating is also suitable here.

Chapter 5 summarize the research in speciation analysis of oxides conducted using LI-TOFMS and discusses the faults or disadvantages in the work. Also, the researches need to be done in the future is suggested.

Key Words: Element Speciation; High irradiance laser ionization; Time-of-Flight Mass Spectrometry; Iron oxides; Cobalt oxides

第一章 前言

1.1 元素形态分析概述

1.1.1 元素形态分析的概念

元素形态是指某种元素的各个物理-化学形态，其总和构成样品中该元素的总浓度^[1]。元素在样品中的物理状态如溶解态、胶体和颗粒状等即为元素的物理形态。而元素在样品中以某种离子或分子存在的实际形式即为元素的化学形态，它是指某一种元素以不同的同位素组成、不同的电子组态或价态以及不同的分子结构等存在的特定形式^[2]。元素的形态分析就是确定元素在样品中的各种形态以及各形态的分布与含量，包括物理形态分析和化学形态分析（如图 1-1）。

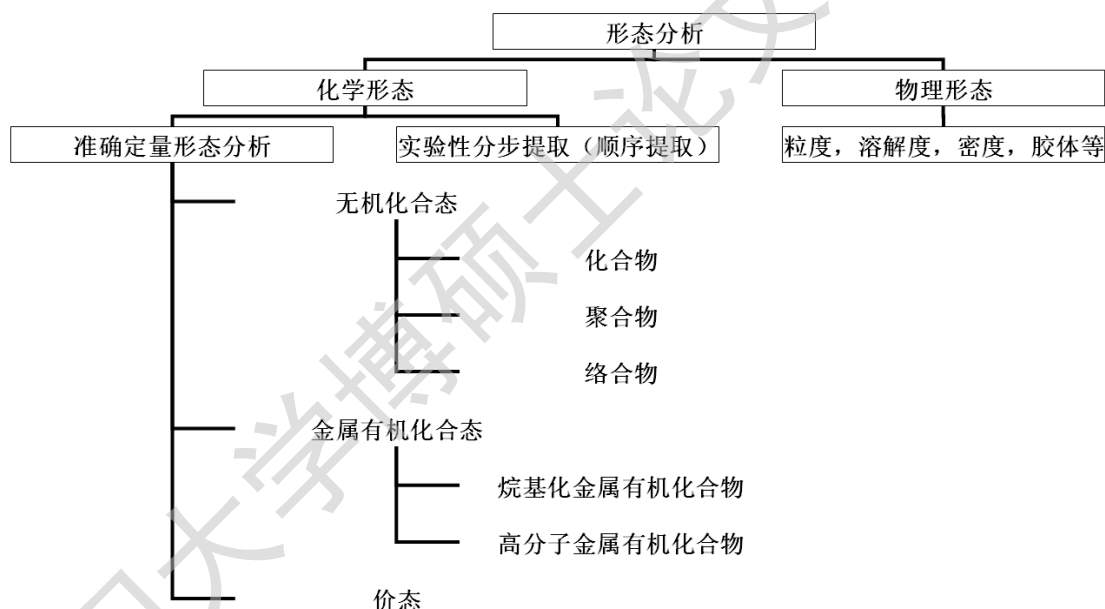


图 1-1 形态分析分类示意图

对于元素化学形态分析，它主要要求能够确定样品中含有的某种特定元素的存在形式（如单质、氧化物、盐类、有机态等），并且定量检测各种形式下的元素含量。为了让人们更加清晰地了解和认识元素化学形态分析，国际纯粹应用化学联合会（IUPAC）于 2000 年统一规定了痕量元素形态分析的定义（IUPAC Guidelines for Terms Related to Speciation of Trace Elements）^[3]：

化学形式（chemical species）：一种元素的特有形式，如：同位素组成，电

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